CATHODIC OXYGEN REDUCTION ON COBALT PHTHALOCYANINE

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Metal phthalocyanine complexes have been reported to have electrocatalytic activity for oxygen reduction in both acidic[1] and basic electrolytes[2] and a patent has been issued for their use in fuel cell electrodes.[3] Since the specific conductance of all phthalocyanines is very low, about 10^{-6} ohm^{-1} cm^{-1}[4] it has been the practice to disperse these compounds in conductive supports in order to utilize their catalytic activity. This renders it impossible to estimate the true specific activity of the phthalocyanine surface or to decide whether their activity is limited by their seemingly prohibitive resistivities. For example if one postulates a phthalocyanine surface which draws a current of 0.2 ma/cm^2, i.e., approximately that obtained from the reduction of oxygen on platinum at 800 mv, a current path length of 1 μ through the phthalocyanine crystal would cause an internal resistance polarization of 2 volts. Under these circumstances any polarization data obtained on phthalocyanine electrodes would reflect the effective electrical contact of the phthalocyanine crystal with the conductive support rather than the transfer resistance of oxygen reduction on the catalyst.

We have examined the electrochemical behavior and activity of a number of thin films of cobalt phthalocyanine in order to separate the resistive and charge transfer components of oxygen reduction and to evaluate the true specific activity of the phthalocyanine surface.

Experimental Part

Cobalt phthalocyanine was prepared by the reaction of cobalt metal with o cyanobenzamide at 250°C.[5] The product was purified by precipitation from concentrated sulfuric acid and sublimation under vacuum. The visible spectrum of the sublimed sample was identical to those in the literature.[6]

Several electrodes were prepared from this material:

a) CoPc was dissolved in concentrated H_2SO_4, mulled with a desired amount of Columbia Neo Spectra carbon or Shawinigan Black, and precipitated on the carbon by dilution in ice water. This resulting powder was mixed with 30% by weight of Teflon 30 dispersion and sprayed on Au plated tantalum screen. Sintering and pressing completed the electrode.

b) CoPc was sublimed onto gold foil under vacuum to form films with loadings of from 0.05 to 0.1 mg/cm^2, although of varying uniformity of thickness.

c) CoPc was adsorbed on Columbia Neo Spectra carbon from pyridine solution. Adsorption isotherms were obtained by measuring the change in concentration of CoPc in solution spectrophotometrically. Conditions were chosen under which a monolayer of phthalocyanine would form on the carbon and catalysts were prepared by filtering the carbon from the pyridine solution after equilibration. The resulting powder was evacuated at 50°C to remove the pyridine and mounted as thin layer[7] electrodes for testing.

Before the adsorption of CoPc, samples of Columbia Neo Spectra carbon (1000 m^2/g) were pretreated in three different ways. The first was heated at 420°C under oxygen to give an acid surface which, on titration with base gave 12 m eq/g of

surface acid species.[8] The second, evacuated at 400°C and exposed to oxygen at room temperature had a basic surface, which had 0.5 m eq/g of basic species. The third was the initial untreated Columbia Neo Spectra carbon.

These electrodes were examined variously in a floating electrode cell,[9] a conventional three compartment cell with gold counter electrode and platinum reference electrode, and as submerged gas electrodes in the manner described for the thin layer electrode.[7]

Results and Discussion

Screen Electrodes

Screen electrodes were first made by method (a) and parameters were varied to give the best possible performance. For instance mechanical mixing of the phthalocyanine and carbon gave poor results relative to a catalyst made by mulling catalyst and support in H_2SO_4. Furthermore, highest activity was displayed by a catalyst to support weight ratio of about 1:1 and the higher surface area Neo Spectra carbon (1000 m^2/g) proved superior to Shawinigan black (70 m^2/g). Data for these comparisons are given in Table I and were obtained from floating electrodes in 50% H_3PO_4.

The effect of each of these variables was such as to suggest that the best performance was achieved when maximum electrical contact was established between the catalyst and the support. Thus the high resistivity of the solid phthalocyanine appeared to limit catalytic activity.

The polarization curve for the best electrode of Table I run in half cell configuration in 30% H_2SO_4 is shown in Figure 1. Since the available surface area of the CoPc was not known, nor the contribution of internal resistance to polarization, no calculation of the intrinsic activity of the CoPc surface could be made.

Table I

W% CoPc[**] in Catalyst Powder	Carbon Support	OCP	O_2 reduction ma at mv[***] 10	100	200
30	Sh. Bk.	755	210	---	---
50	Sh. Bk.	789	410	310	260
70	Sh. Bk.	760	345	220	---
30	Sh. Bk.[*]	802	148	---	---
50	N. Sp.	750	570	360	260

Films of CoPc on Gold

If the major portion of the polarization of phthalocyanine electrodes were caused by the internal resistance then the cathodic reduction of oxygen on thin films of CoPc on gold would be inversely proportional to film thickness. As is shown in Table II this effect was not observed for films of phthalocyanine sublimed onto gold foil. The current density at a given voltage appeared to be independent of film thickness. Moreover when an electronic interrupter measurement was made on the film no sharp jump characteristic of internal resistance was seen. In agreement with these observations the activation energy for oxygen reduction on this film was calculated from experiments at several temperatures to be less than 15 K cals/mole

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[*]Mechanically mixed. All others mulled in H_2SO_4.
[**]Electrode contains 30% TFE.
[***]50 W% H_3PO_4, 70°C.

whereas the activation energy for intrinsic semi-conduction in CoPc, the expected value if conductance limits performance, has been measured as 36 K cals/mole.[4]

Table II

Oxygen Reduction on Films of CoPc of Varying Thickness on Gold

Film Thickness[*] ma/cm^2	O_2 Reduction[**] μa at 500 mv
.01	17
.05	4
.58	8

The apparently contradictory results obtained from screen electrodes and CoPc films might be reconciled if one assumed that the films of CoPc were porous and that, due to high internal resistance, oxygen reduction only took place at the bottom of the pores, where phthalocyanine was in good electrical contact with the gold foil base. Then no internal resistance would be observed although a large gas concentration polarization might be expected in the pores. The porous nature of these films was proven by electrodepositing gold and copper on them. Thus, although the plating current was kept constant no deposit was visible except towards the end of the experiment when microscopic metallic beads appeared on the surface.

The CoPc films were also investigated by cyclic voltammetry under N_2 at scan rates of 410 mV/sec. The CoPc film disintegrated rather rapidly in the electrolyte if the electrode was polarized to low potentials ($E^* = 0$ to 50 mv versus S.H.E. in same medium). The samples were therefore kept at $E^* \geq 300$ mv. Under the conditions used the currents were due within a few percent solely to reactions of the electrode material, i.e., CoPc.

Progressive changes which occurred on repeated cycling of a characteristic film are shown in Figure 2. We see initially (Curve A) two redox systems designated by I and II with equilibrium potentials of approximately $E_I^* = 900$ mv and $E_{II}^* = 700$ mv. The original red-purple electrode color remained the same during the first potential cycles. These curves rapidly changed during subsequent cycles, the change being the more rapid the thinner was the film. An intermediate state was reached, character-ized by curve B in Figure 2, and by a clear blue color at low, and the former red-purple color at high potentials. Eventually a new couple III appeared at around $E_{III}^* = 450$ mv which became the dominant feature. Simultaneously the color changed to grass green (at potentials cathodic to peak III) and purple (at higher potentials) without any blue intermediate. It is probable that the reactions involved in these couples are the redox reactions of central Co ion involving the valencies 3+, 2+, 1+ and zero.[10] The measured resistance of the dry film was approximately 4000 to 5000 Ω cm^2 corresponding to a specific resistivity of $\sigma \simeq 10^8$ Ω cm. The maximum currents in Figure 2 (curve C) are 4.5 ma/cm^2 and these peaks are separated by 50 mv. The IR loss within the film therefore could not be larger than $50/2 = 25$ mv. If the original resistivity were maintained during the experiment the thickness λ of the layer involved in reaction III would have to be thinner than approximately $\lambda \simeq Ra/\sigma \simeq 25/4.5 \times 10^{-8} \simeq 5\text{\AA}$. A calculation based on the density of CoPc shows that a layer this thin can produce a charge of only 0.01 μ Coul/cm^2 whereas the total area within the Curve C of Figure 2 indicates that changes two orders of magnitude greater are involved (Table III). These changes, in Table III, would be consistent with the case where approximately 20% of the thickness of the CoPc film was involved in the redox reaction. One must therefore conclude that the resistiv-ity of the CoPc breaks down as a load is applied to the electrode film and that the operating resistances of the film are lower than those measured in the dry state.

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[*]Prepared by sublimation.
[**]Tafel slope approximately 160 mv.

Table III

Coulometric Behavior of CoPc Films during Cyclic Voltammetry

CoPc Loading [mg/cm^2]	Area [m Coul/cm^2]	Charge [Coul/mole CoPc]
.055	5.8	6.0 x 10^4
.075	5.9	4.5 x 10^4
.095	4.9	3.0 x 10^4

The electrical circuit at the CoPc/electrolyte interface has to be completed by Faradaic reaction since capacity currents would not be sufficiently large. For this role we assume H$^+$ ions to be the most likely reactant according to the diagram:
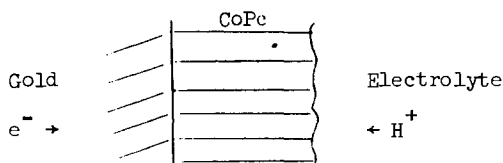
Without supply of H$^+$ into CoPc the reaction could not proceed even if electronic conductance were sufficient. Hence the reduction of the cobalt ion requires the formation of the protonated form of phthalocyanine (free-base). The model which emerges from these arguments, which can explain at least some of the observations is as follows: The CoPc in contact with the electrolyte acquires electronic conductivity by the passage of protons from the electrolyte however due to limited ion-conductivity only a fraction can react during a voltammetric cycle.

The catalytic activity of the CoPc films on gold is therefore a complex combination of reaction at the bottom of pores in the film and extending into the film because of the increased conductance of phthalocyanine under load. It is thus not possible to evaluate the true specific activity of the phthalocyanine surface from polarization data on these thin films.

Formation and Catalytic Activity of CoPc Monolayers

Cobalt phthalocyanine adsorbed strongly from pyridine solution onto carbon. The equilibrium concentration of phthalocyanine in solution was measured spectroscopically and the concentration on the surface of the carbon calculated by the difference. The adsorption isotherms are shown for the three different carbon surfaces in Figures 3, 4 and 5. These have the sharp elbow and saturation coverage characteristic of Langmuir adsorption and indeed the isotherms may be plotted according to the linear form of the Langmuir isotherm[11] (Figures 6, 7 and 8).

$$\frac{C_B}{C_S} = \frac{C_B}{C_M} = \frac{1}{KC_M}$$

C_B = concentration of CoPc in solution (mg/liter)
C_S = concentration of CoPc on surface (mg CoPc/mg carbon)
C_M = surface concentration at saturation coverage
K = adsorption equilibrium constant

The saturation coverages for each carbon surface were very similar, Table IV, suggesting that in strongly basic pyridine solution differences in surface species was minimized. The surface area occupied by one CoPc molecule at saturation coverage is also listed and shows that the CoPc was considerably less than close packed since

the CoPc molecule is approximately 180 $Å^2$. It is unlikely that the very small carbon particles, < 30 Å diameter, have pores sufficiently large to occlude the CoPc molecules therefore we assume the CoPc to be dispersed on the surface of the carbon and in strong interaction with it.

Table IV

Saturation Coverage of CoPc adsorbed from
Pyridine Solution on Various Neo Spectra Carbon Surfaces

Surface Pretreatment	Saturation Coverage mg CoPc/mg Carbon	Surface Area per CoPc Molecule $Å^2$
Untreated	0.107	880
Acidic	0.135	700
Basic	0.141	670

Since CoPc is insoluble in 20% H_2SO_4 it was possible to use these preparations in electrodes for oxygen reduction. Thus the activity for oxygen reduction of monolayers of CoPc could be measured; a condition where there is no possible resistance to the passage of electrons from the conductive support to the active site and hence where internal resistance should be negligible.

The catalyst powders were mounted in thin layer electrodes[7] designed to eliminate gas concentration polarization and electrolyte IR losses. Polarization curves for oxygen reduction on phthalocyanine supported on the three different carbon surfaces are shown in Figures 9, 10, 11. The linearity of the Tafel plot and its lack of dependence on catalyst loading confirms that these data refer only to charge transfer.

The current density, plotted as ma/mg CoPc, was very nearly the same for each of the three carbon surfaces and only slightly greater than for the carbon without CoPc (Figure 12). Since the phthalocyanine was spread as a monolayer the exchange current could be calculated assuming 180 $Å^2$ per phthalocyanine molecule. This gave a value of 4×10^{-11} amps/cm^2 for i_o and a Tafel slope of 160 mv for CoPc on the acid carbon surface. The other surfaces were not significantly different. Thus the CoPc surface is rather weakly catalytic; only slightly better than the carbon on which it is supported. The presence of different surface species under the adsorbed phthalocyanine appears to have little effect on the catalytic activity although the basic carbon surface seems to lower the activity slightly.

Polarization data for the best screen electrode made from CoPc by method (a) is also plotted on the basis of ma/mg CoPc in Figure 9 for comparison. Its lower performance points out that this electrode did not make the most efficient use of the phthalocyanine on the carbon possibly because all the phthalocyanine was not in electrical contact with the support.

Discussion

Cyclic voltammetry of the thin films of phthalocyanine showed that the resistance of the phthalocyanine decreased at cathode potentials as the oxidation state of the central ion changed. Hence despite the very high initial resistance of phthalocyanine there is probably not an important resistance contribution to cathode polarization. This behavior would imply that the activity of cobalt phthalocyanine mixed with a conductive support in a screen electrode should be close to the intrinsic activity of the available phthalocyanine. This assumption is borne out by the very similar activity of thin layer electrodes with monolayers of phthalocyanine and the screen electrodes in Figure 9.
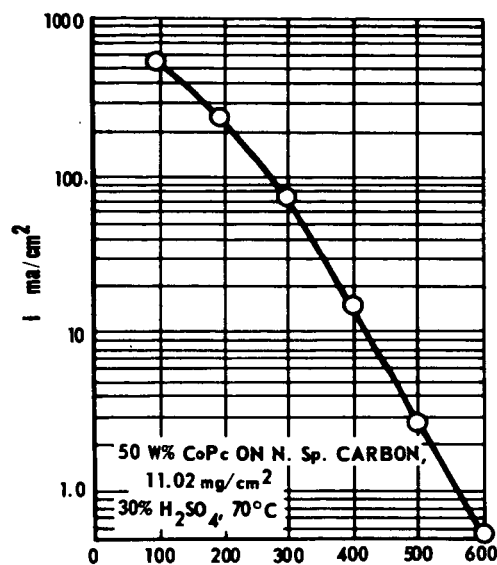
.Undoubtedly the nature of the surface in which the phthalocyanine is supported may have a large effect on its activity and therefore some support other than carbon may be found giving enhanced activity. Indeed the crystalline morphology of the phthalocyanine itself is known to affect catalytic activity of a number of phthalo-cyanines for the decomposition of formic acid.[12] Moreover the mechanism for the reduction of oxygen on a semi-conductor surface will certainly be complicated by changes in the electronic structure of the central metal ion. However the present study demonstrates that electronic conductance through the semi-conductor is not a limitation in the case of cobalt phthalocyanine but that the electrochemical reaction at the catalyst surface is the slow process.

References

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(4) W. Felmayr and I. Wall, J. Elect. Soc., 105, 141 (1958).

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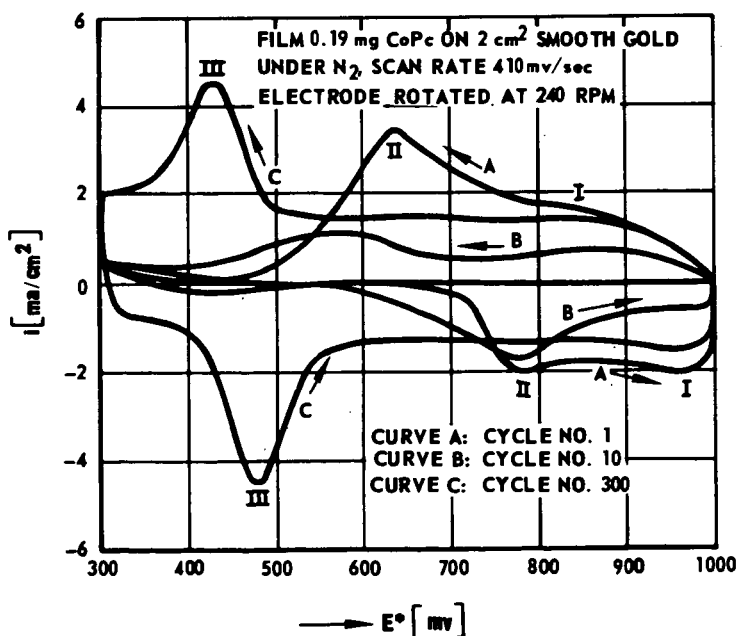(12) W. Hanke, Natur wissenschafter, 52, 475 (1965).

Figure 1
OXYGEN REDUCTION ON CoPc SUPPORTED
ON NEO SPECTRA CARBON IN A SCREEN ELECTRODE

50 W% CoPc ON N. Sp. CARBON,
11.02 mg/cm²
30% H_2SO_4, 70°C

E mv (VS SHE)

Figure 2
CYCLIC VOLTAMMETRY OF CoPc FILM
SUBLIMED ON GOLD

FILM 0.19 mg CoPc ON 2 cm² SMOOTH GOLD
UNDER N_2, SCAN RATE 410 mv/sec
ELECTRODE ROTATED AT 240 RPM

CURVE A: CYCLE NO. 1
CURVE B: CYCLE NO. 10
CURVE C: CYCLE NO. 300

E^0 [mv]

Figure 3

ADSORPTION ISOTHERM CoPc
ON UNTREATED NEO SPECTRA CARBON

C_B CONCENTRATION OF CoPc IN PYRIDINE SOLUTION mg/ℓ

C_S CONCENTRATION OF CoPc ON CARBON SURFACE mg/mg

C_B mg/ℓ
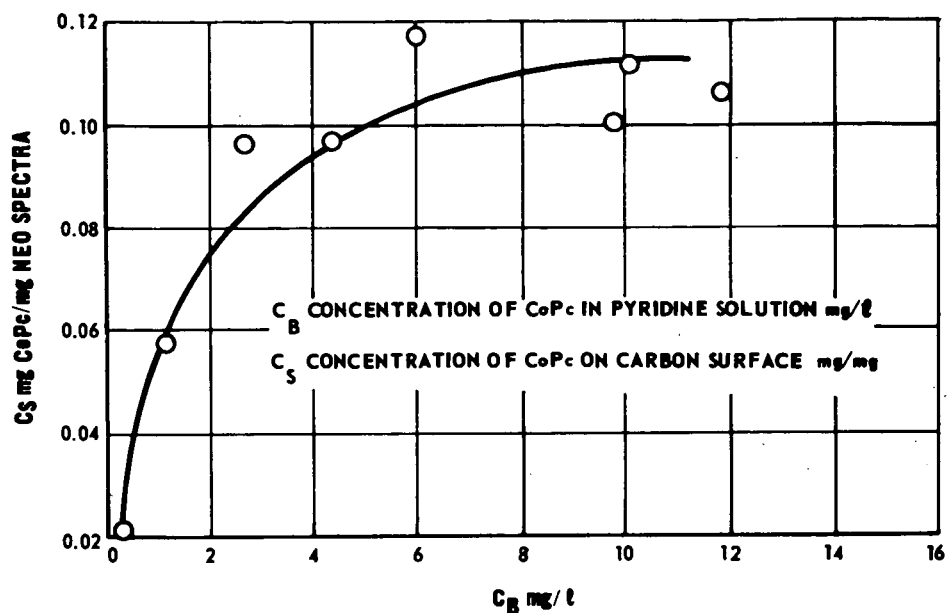
Figure 4

ADSORPTION ISOTHERM CoPc ON ACID NEO SPECTRA

C_B CONCENTRATION OF CoPc IN PYRIDINE SOLUTION mg/ℓ

C_S CONCENTRATION OF CoPc ON CARBON SURFACE mg/mg

C_B mg/ℓ
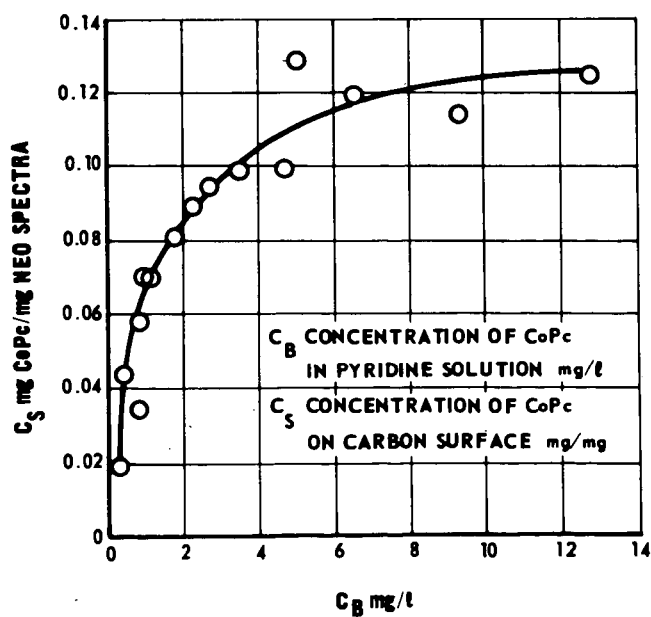
Figure 5

ADSORPTION ISOTHERM CoPc
ON BASIC NEO SPECTRA CARBON

C_B CONCENTRATION OF CoPc IN PYRIDINE SOLUTION mg/ℓ

C_S CONCENTRATION OF CoPc ON CARBON SURFACE mg/mg

C_S mg CoPc/mg NEO SPECTRA

C_B mg/ℓ
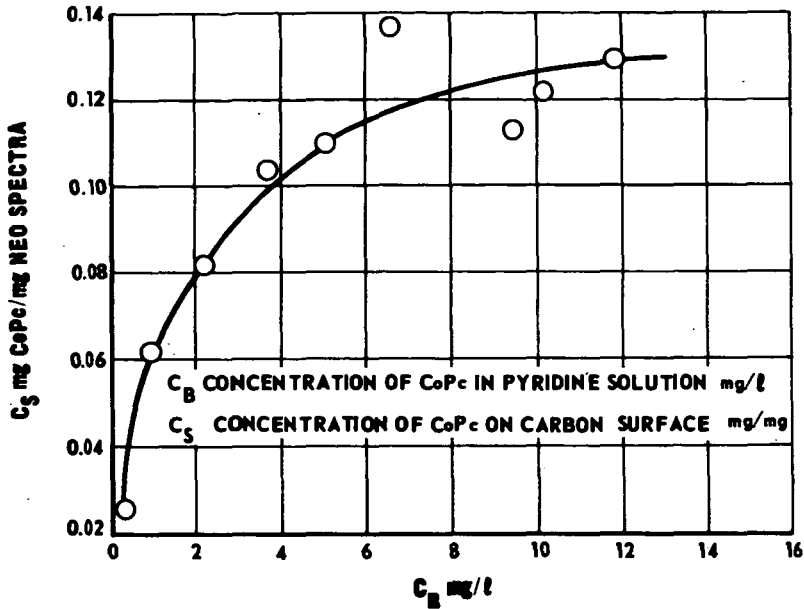
Figure 6

LANGMUIR ISOTHERM CoPc
ON UNTREATED NEO SPECTRA

C_B/C_S

C_B CONCENTRATION OF CoPc IN PYRIDINE SOLUTION mg/ℓ

C_S CONCENTRATION OF CoPc ON SURFACE OF CARBON mg/mg

SATURATION COVERAGE 0.107 mg CoPc/mg CARBON

C_B mg/ℓ

53
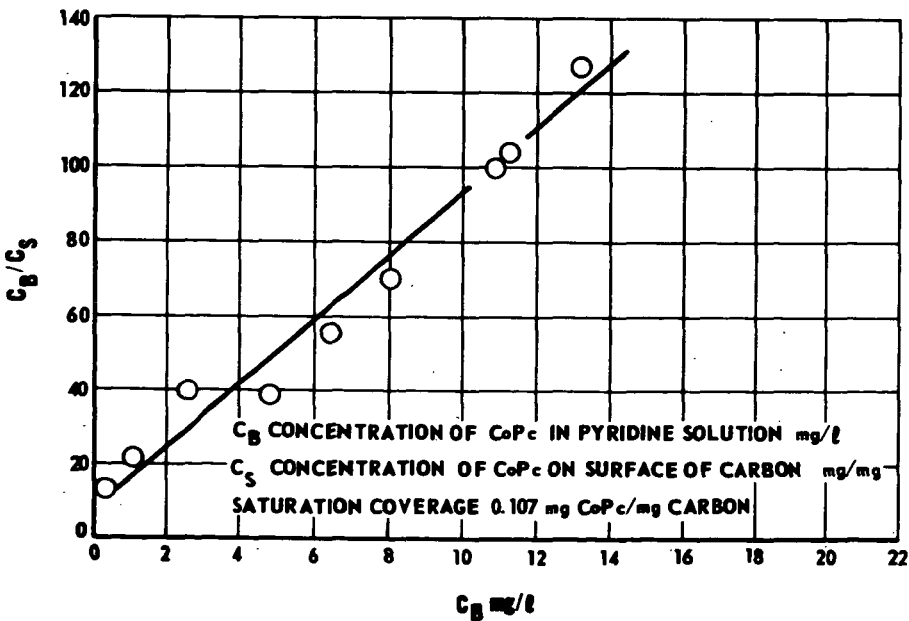
Figure 7

LANGMUIR ISOTHERM CoPc
ON ACID NEO SPECTRA CARBON

C_B CONCENTRATION OF CoPc IN PYRIDINE SOLUTION mg/ℓ

C_S CONCENTRATION OF CoPc ON CARBON SURFACE mg/mg

SATURATION COVERAGE = 0.135 mg CoPc/mg CARBON

C_B mg/ℓ
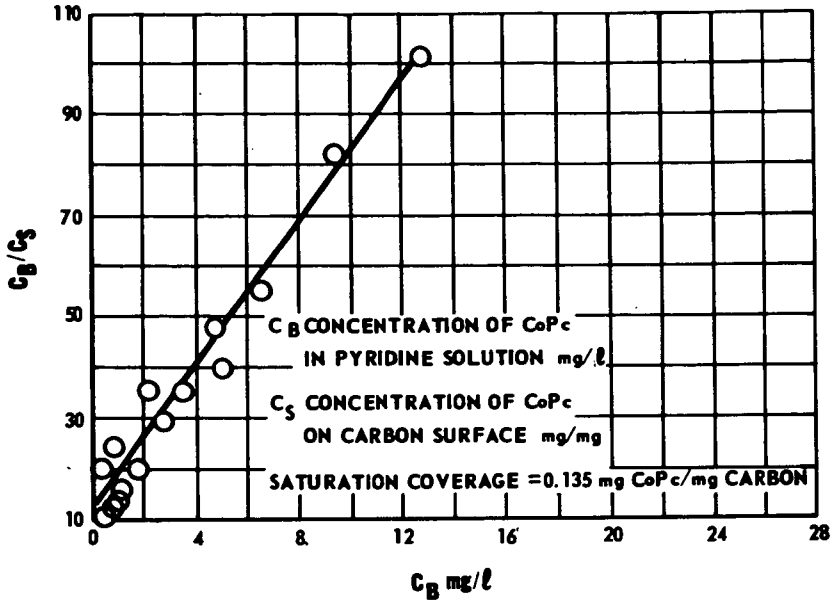
Figure 8

LANGMUIR ISOTHERM CoPc
ON BASIC NEO SPECTRA CARBON

C_B CONCENTRATION OF CoPc IN PYRIDINE SOLUTION mg/ℓ

C_S CONCENTRATION OF CoPc ON CARBON SURFACE mg/mg

SATURATION COVERAGE = 0.141 mg CoPc/mg CARBON

C_B
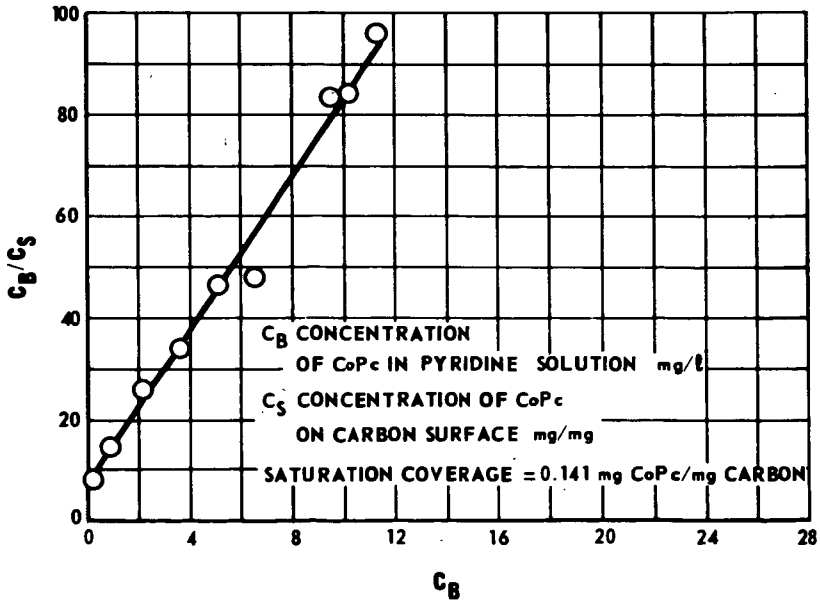
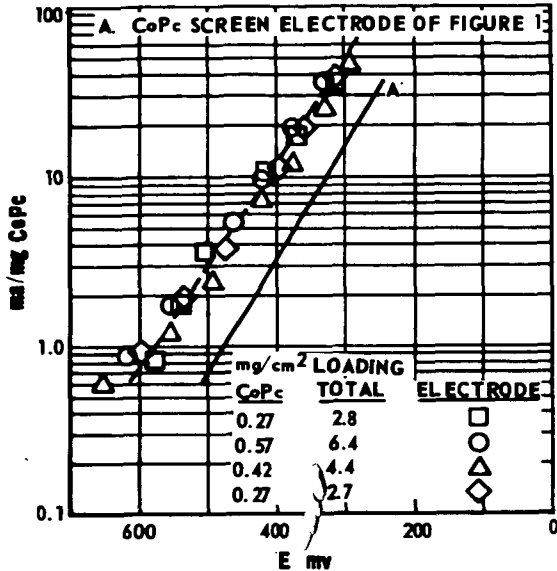# Figure 9: CATHODIC OXYGEN REDUCTION ON CARBON SUPPORTED CoPc MONOLAYERS (UNTREATED NEO SPECTRA)

50°C, 20% H_2SO_4 0.95 mg CoPc/mg NEO SPECTRA

CoPc ON UNTREATED NEO SPECTRA

Figure 10: CATHODIC OXYGEN REDUCTION ON CARBON SUPPORTED CoPc MONOLAYERS (ACID NEO SPECTRA)

50°C, 20% H_2SO_4 0.11 mg CoPc/mg NEO SPECTRA
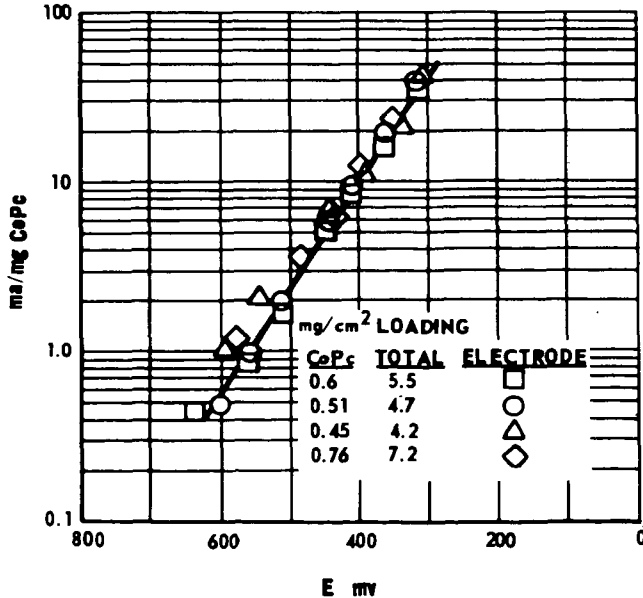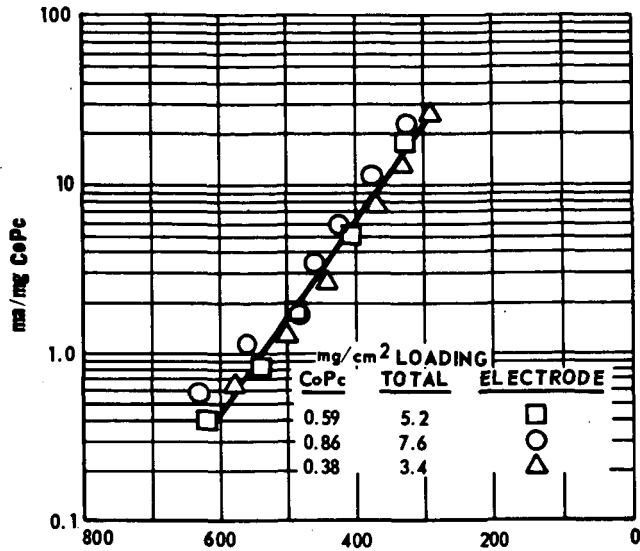
CoPc ON ACID NEO SPECTRA CARBON

Figure 11: CATHODIC OXYGEN REDUCTION ON CARBON
SUPPORTED CoPc MONOLAYERS (BASIC NEO SPECTRA)

50°C, 20% H_2SO_4

CoPc ON BASIC NEO SPECTRA

0.11 mg CoPc/mg NEO SPECTRA

mg/cm² LOADING		
CoPc	TOTAL	ELECTRODE
0.59	5.2	□
0.86	7.6	○
0.38	3.4	△

E mv

Figure 12

OXYGEN REDUCTION ON UNTREATED NEO SPECTRA
CARBON WITH AND WITHOUT ADSORBED CoPc

50°C, 20% H_2SO_4

NEO SPECTRA CARBON

mg/cm² LOADING

CoPc	TOTAL	ELECTRODE
0	2.0	◁
0	4.6	○
0	4.8	◇
0.27	2.8	◇
0.57	6.4	▽
0.42	4.4	△
0.27	2.7	□

E mv